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"Transition Organometallic Heterobimetallic  
 $\mu$ -Carbon Dioxide and  $\mu$ -Format Complexes in  
Homogeneous Carbon Dioxide Fixation"

Alan R. Cutler, Principal Investigator

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<p>New W- and Re-containing bimetallic <math>\mu</math>-formate salts <math>[L_xM]-OCHO-[ML_y]^+</math> (<math>L_xM</math>, <math>L_yM = W(CO)_3Cp</math>, <math>Re(NO)(CO)Cp</math>) were characterized. The Re center is more labile than the corresponding W center. Their reactions with nucleophiles, especially hydride donors, were studied. Attempts to synthesize bimetallic <math>CO_2</math> complexes <math>Cp(CO)_2Fe-CO_2-M''L_y</math> from <math>Fp-CO_2^-</math> and a variety of organometallic Lewis Acids <math>LyM''^+</math> were unsuccessful. The stable (<math>\eta^1-C : \eta^2-S,S'</math>) <math>CS_2</math> adduct <math>Fp-C(S)S-Fp</math>, prepared from <math>FpCS_2^-</math>, was characterized. Early-late bimetallic <math>\mu-(\eta^1-C : \eta^2-O,O')</math> <math>CO_2</math> complexes <math>Cp(CO)_2M-CO_2-M'(Cl)Cp_2</math> (<math>M = Fe, Ru</math>; <math>M' = Ti, Zr, Hf</math>) were synthesized (from <math>FpCO_2^-</math> or <math>RpCO_2^-</math>) and studied. Cleavage of a C-O bond on the bridging <math>CO_2</math> is a prevailing trend in (1) thermal decomposition of these bimetallocarboxylates (stability decreases: <math>RuZr \gg FeZr &gt; RuTi &gt; FeTi</math>), (2) protonation of the more stable Zr adducts and (3) <math>Cp_2Zr(H)Cl</math> reduction of the fully characterized <math>RuZr CO_2</math> adduct to the <math>\mu(\eta^1-C : \eta^1-O)</math> formaldehyde complex <math>Rp-CH_2O-Zr(Cl)Cp_2</math>. <math>CO_2</math> converts the Fe-Zr and Ru-Zr bimetallics <math>Cp(CO)_2M-Zr(X)Cp_2</math> (<math>X = Cl, O^tBu</math>) to their bimetallocarboxylates.</p>					
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## Part I

- b. "Carbon Monoxide and Carbon Dioxide Fixation: Relevant  $C_1$  and  $C_2$  Ligand Reactions Emphasizing  $(\eta^5-C_5H_5)Fe$ -Containing Complexes", A. R. Cutler, P. K. Hanna, and J. C. Vites, *Chem. Rev.* **1988**, *88*, 1363 (Invited).<sup>‡</sup>
- "Homo- and Hetero-Bimetallic  $\mu(\eta^1-O:\eta^1-O')$  Formate Complexes  $(M-OCHO-M')^+ PF_6^-$  [ $M, M' = (\eta^5-C_5H_5)(CO)(NO)Re, (\eta^5-C_5H_5)(CO)_3W$ , and  $(\eta^5-C_5H_5)(CO)_2Fe$ ], Their Synthesis, Solution Lability, and Reactivity Towards Hydride Donors", C. C. Tso and A. R. Cutler, *Inorg. Chem.* **1990**, *29*, 471.\*
- "Reactions of Carbon Disulfide and Carbon Dioxide Adducts  $(\eta^5-C_5H_5)(CO)_2Fe-CX_2^-$  with Organoiron Electrophiles", M. E. Giuseppetti-Dery, B. E. Landrum, J. L. Shibley, and A. R. Cutler, *J. Organomet. Chem.* **1989**, *378*, 421.\*
- "Characterization of the Heterobimetallic  $\mu(\eta^1-C:\eta^2-O,O')$  Carbon Dioxide Complexes  $Cp(CO)_2M-C(O)O-M'(Cl)Cp_2$  ( $M = Fe, Ru; M' = Ti, Zr$ )", J. C. Vites, M. E. Giuseppetti-Dery, and A. R. Cutler, *Organometallics* **1991**, *10*, 2827.
- "Reduction of the Heterobimetallic  $\mu(\eta^1-C:\eta^2-O,O')$  Carbon Dioxide Complex  $Cp(CO)_2Ru-C(O)O-Zr(Cl)Cp_2$  to its  $\mu(\eta^1-C:\eta^1-O)$  Formaldehyde Derivative  $Cp(CO)_2Ru-CH_2O-Zr(Cl)Cp_2$ : Hydride Transfer Occurs at Ligated Carbon Monoxide", B. D. Steffey, J. C. Vites, and A. R. Cutler, *Organometallics* **1991**, *10*, 3432.
- e. ONR Technical Report No. 4: "Characterization of a Family of Heterobimetallic  $\mu(\eta^1-C:\eta^2-O,O')$  Carbon Dioxide Complexes  $Cp(CO)_2M-C(O)O-M'(Cl)Cp_2$  ( $M = Fe, Ru; M' = Ti, Zr$ )", J. C. Vites, M. E. Giuseppetti-Dery, and A. R. Cutler
- h. "Catalyzed and Noncatalyzed Hydrosilation of Metal Acyl Complexes," New England Workshop on Organometallic Chemistry, Andover, MA (May 5-7, 1989).<sup>‡</sup>
- Office of Naval Research / Gas Research Institute Conference on Carbon Dioxide Reactivity; Stanford Research Institute (Menlo Park, CA) 1988; "Heterobimetallic Carbon Dioxide Complexes and  $CO_2$  Reduction."
- Second International Conference on Heteroatom Chemistry (SUNY-Albany) 1989  
North East Regional ACS meeting, June 20, 1989; "Heterobimetallic Carbon Dioxide Complexes and  $CO_2$  Reduction."
- Miami National ACS meeting, September, 1989, "Heterobimetallic Carbon Dioxide Complexes and  $CO_2$  Reduction."

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- e. Significant Results .....page 5
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# Transition Organometallic Heterobimetallic $\mu$ -Carbon Dioxide Complexes in Homogeneous Carbon Dioxide Fixation

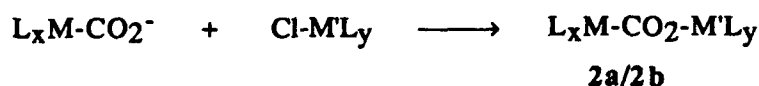
## Project Description

We are establishing the coordinated ligand reactions depicted for reducing CO<sub>2</sub> to formaldehyde and methanol; our objective in future studies includes optimizing and combining these ligand reactions into a reaction cycle or a catalytic system.

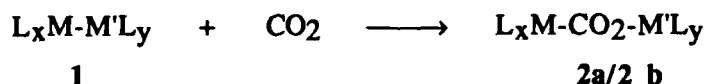
Our approach exploits bimetallic complexation of CO<sub>2</sub> and uses a third metal system as the reductant (e.g., catalytic hydrosilation). These bimetallic CO<sub>2</sub> adducts **2** feature synergistic CO<sub>2</sub> binding in which an electron-rich metal system L<sub>x</sub>M contributes ( $\eta^1$ -C) metallocarboxylate binding and an oxophilic L<sub>y</sub>M' system sequesters one or both metallocarboxylate oxygens (**2a** and **2b**, respectively). In addition to stabilizing the CO<sub>2</sub> adduct, the resulting electronic "push-pull" also activates the CO<sub>2</sub> ligand as a hydride acceptor.

## Goals

### I. Synthesis and characterization of heterobimetallic CO<sub>2</sub> complexes



### II. CO<sub>2</sub> "insertion" into the metal-metal bond of **1** (step A)



### III. Reduction of ligated CO<sub>2</sub> to heterobimetallic formaldehyde compounds **4** (step B)



### IV. Reaction chemistry of the formaldehyde compounds L<sub>x</sub>M-CH<sub>2</sub>O-M'L<sub>y</sub> (**4**)

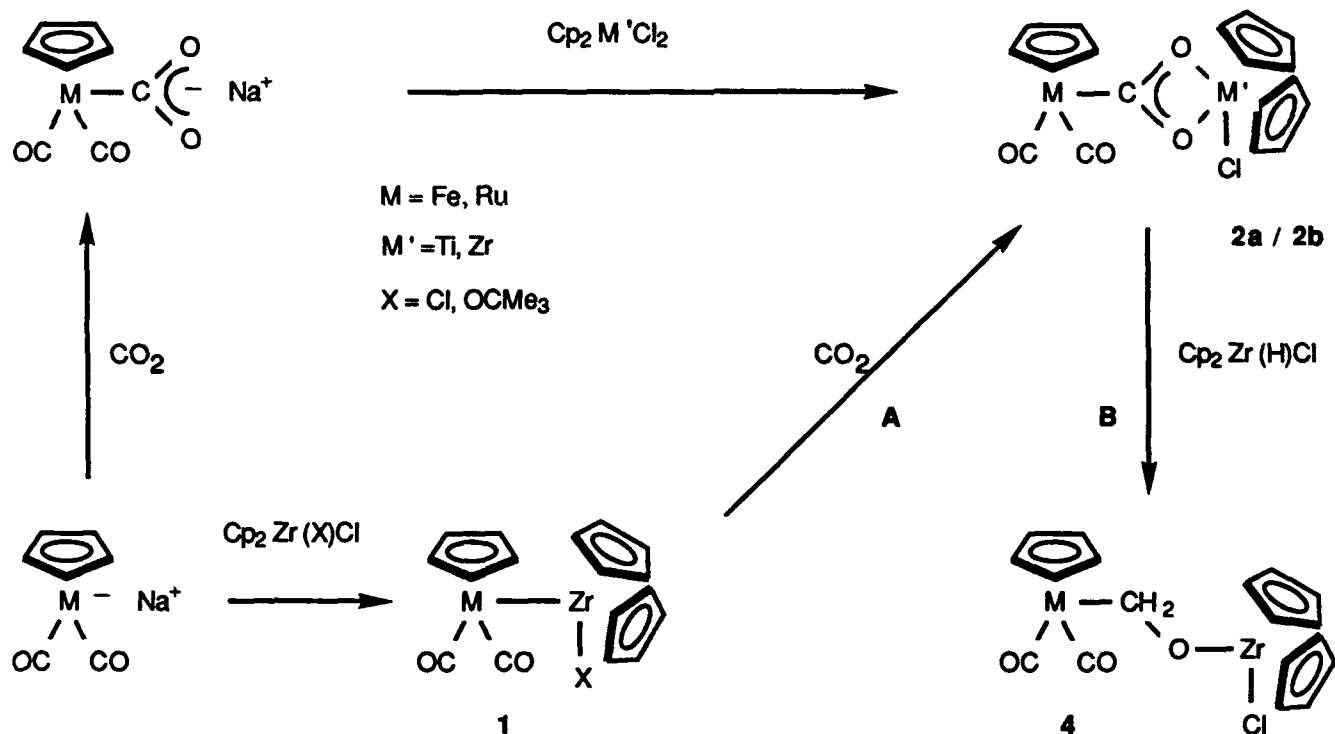
- (a) Further reduction : L<sub>x</sub>M-CH<sub>2</sub>O-M'L<sub>y</sub>  $\longrightarrow$  L<sub>x</sub>M-CH<sub>3</sub>,
- (b) Formaldehyde extrusion (step C) [formaldehyde + base  $\rightarrow$  Formose liquid]

### V. Electrochemical studies

- (a) Electron-transfer catalysis: enhance lability of L<sub>x</sub>M-M'L<sub>y</sub> (**1**) (step A) and of L<sub>x</sub>M-CH<sub>2</sub>O-M'L<sub>y</sub> (**4**) (step B)
- (b) Electrochemistry of CO<sub>2</sub> adducts L<sub>x</sub>M-CO<sub>2</sub>-M'L<sub>y</sub> (**2**) as model for electro-catalytic CO<sub>2</sub> reduction on electrode surface

# Transition Organometallic Heterobimetallic $\mu$ -Carbon Dioxide Complexes in Homogeneous Carbon Dioxide Fixation

## RESULTS



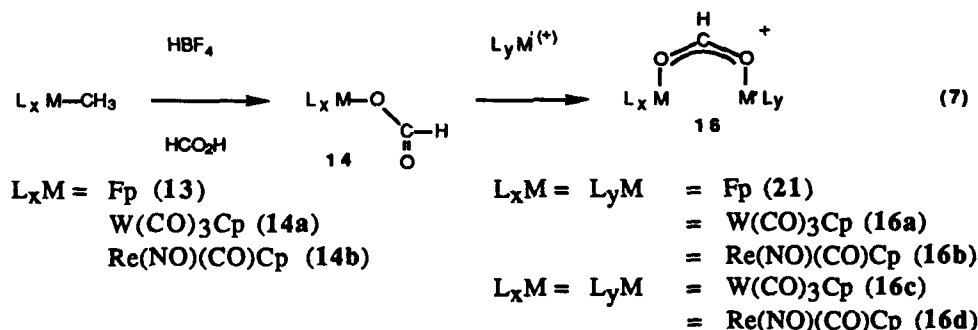
- I. Stability of these heterobimetallic  $\text{CO}_2$  complexes **2a/2b** as a function of  $\text{M}$  and  $\text{M}'$ :  
 $\text{RuZr} \gg \text{FeZr} > \text{RuTi} > \text{FeTi}$  (relative ease of synthesis & purification)  
 Equilibrium **2a** and **2b**: established for  $\text{Cp}(\text{CO})_2\text{Ru}-\text{CO}_2-\text{Zr}(\text{OCMe}_3)\text{Cp}_2$   
 and  $\text{Cp}(\text{CO})_2\text{Ru}-\text{CO}_2-\text{Zr}(\text{Cl})(\text{C}_5\text{Me}_2)_2$
- II.  $\text{CO}_2$  "insertion" into the metal-metal bond,  $\mathbf{1} \longrightarrow \mathbf{2a/2b}$  (step A)  
 Rate (lability) as a function of  $\text{M}$  ( $\text{X}$  on  $\text{Zr} = \text{Cl, OCM}_3$ ):  
 $\text{Cp}(\text{CO})_2\text{Fe}-\text{CO}_2-\text{Zr}(\text{Cl})\text{Cp}_2 \gg \text{Cp}(\text{CO})_2\text{Ru}-\text{CO}_2-\text{Zr}(\text{X})\text{Cp}_2$
- III. Reduced ligated  $\text{CO}_2$  to yield heterobimetallic formaldehyde compounds **4** (step B)  
 Characterized  $\text{Cp}(\text{CO})_2\text{M}-\text{CH}_2\text{O}-\text{Zr}(\text{Cl})\text{Cp}_2$  (**4**)  $\text{M} = \text{Fe, Zr}$

# Transition Organometallic Heterobimetallic $\mu$ -Carbon Dioxide and $\mu$ -Formate Complexes in Homogeneous Carbon Dioxide Fixation

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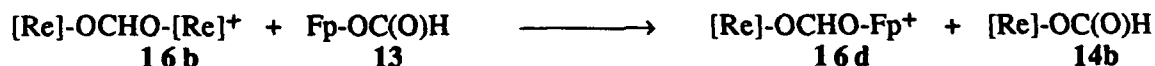
## A. Bridging Formate Chemistry

We finished our studies on the synthesis and characterization of homo- and heterobimetallic bridging formates and on their reductive chemistry. New tungsten-

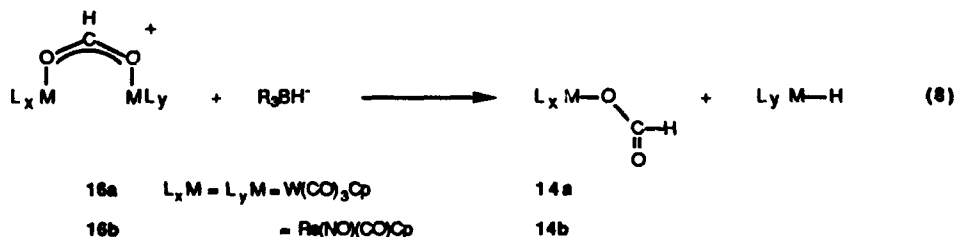


and rhenium-containing  $\eta^1$ -O formates **14a** and **14b** and their bimetallic  $\mu$ -formate salts **16a-16d** were synthesized and were fully characterized. The reactions of nucleophiles, especially hydride donors, with **16a-16d** received considerable emphasis.

Rhenium- and tungsten-containing  $\mu$ -formate compounds differ greatly in their solution chemistry. Bis-Re **16b**, in particular, proves to be unusually labile: a rhenium center on the bimetallic formates **16b** and **16d** is considerably more labile than the corresponding tungsten center on **16a** and **16c**.



Both  $\mu$ -formates **16a** and **16b** react identically with one equivalent of  $\text{LiHBEt}_3$  or  $\text{KHB(Oi-Pr)}_3$  and immediately release a formate complex (**14a** or **14b**, respectively) (eq. 8). Hydride transfer to **16a** with  $\text{LiDBEt}_3$  eliminated only  $\text{Cp(CO)}_3\text{W-OC(O)H}$  (**14a**)



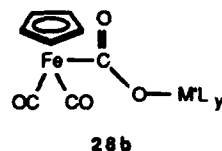
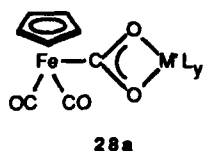
## B. Bimetallic CO<sub>2</sub> Complexes

### 1. Late-Late Bimetal Combinations

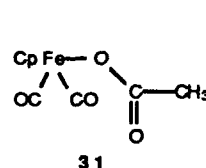
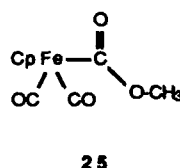
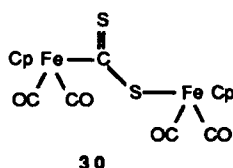
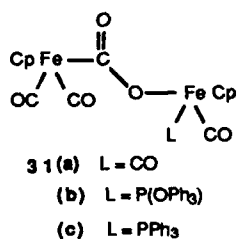
We attempted to synthesize examples of bimetalloxy-carboxylates **28a** and **28b** by treating  $\text{Fp-CO}_2^-$  (**24**) with organometallic Lewis Acid  $\text{LyM}^+ / \text{LyM-X}$ . Lewis acids such as



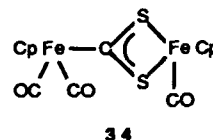
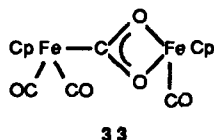
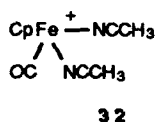
$\text{Fp}(\text{THF})^+\text{PF}_6^-$ ,  $\text{Cp}(\text{L})(\text{CO})\text{FeI}$  ( $\text{L} = \text{CO}$ ,  $\text{PPh}_3$ ,  $\text{P}(\text{OPh})_3$ ),  $\text{FpX}$  ( $\text{X} = \text{Cl}$ ,  $\text{I}$ ,  $\text{OSO}_2\text{CF}_3$ ,  $\text{HgCl}$ ), and etc.



Although these attempts proved unsuccessful, we did highlight the dramatic differences between  $\text{FpCO}_2^-$  (24) and  $\text{FpCS}_2^-$  (29) in their reactions with organoiron electrophiles. No examples of bis-iron  $\mu(\eta^1\text{-C} : \eta^1\text{-O}) \text{CO}_2$  complexes 31 were observed, in contrast to the

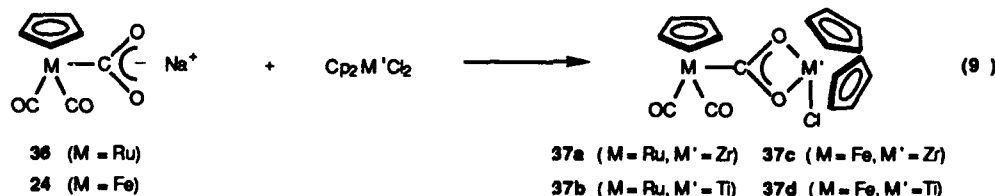


thermally stable  $(\eta^1\text{-C} : \eta^1\text{-S}) \text{CS}_2$  adduct  $\text{Fp-C(S)S-Fp}$  (30). Treatment of 29 with  $\text{Cp}(\text{CO})\text{Fe}(\text{NCCH}_3)_2^+ \text{PF}_6^-$  (32) affords the stable, fully characterized  $(\eta^1\text{-C} : \eta^2\text{-S,S'}) \text{CS}_2$  complex 34, whereas the analogous reaction using  $\text{FpCO}_2^-\text{Na}^+$  (24) decomposes.



## 2. Early-Late Bimetallic $\mu\text{-CO}_2$ Compounds

Our study on using the new metallocarboxylate  $\text{Cp}(\text{CO})_2\text{Ru-CO}_2^-\text{Na}^+$  ( $\text{RpCO}_2^-\text{Na}^+$ ) (36) and its known iron congener  $\text{FpCO}_2^-\text{Na}^+$  (24) to generate the family of  $\text{RuZr}$ ,  $\text{RuTi}$ ,  $\text{FeZr}$ , and  $\text{FeTi}$  bimetallic  $\text{CO}_2$  adducts 37a-37d (eq. 9) is complete. This work emphasizes the relative ease of synthesis and stability of 37a-37d, as well as deduction of their structures from  $^1\text{H}$  and  $^{13}\text{C}$  NMR and IR spectral data. We also find that cleavage of a carbon-oxygen

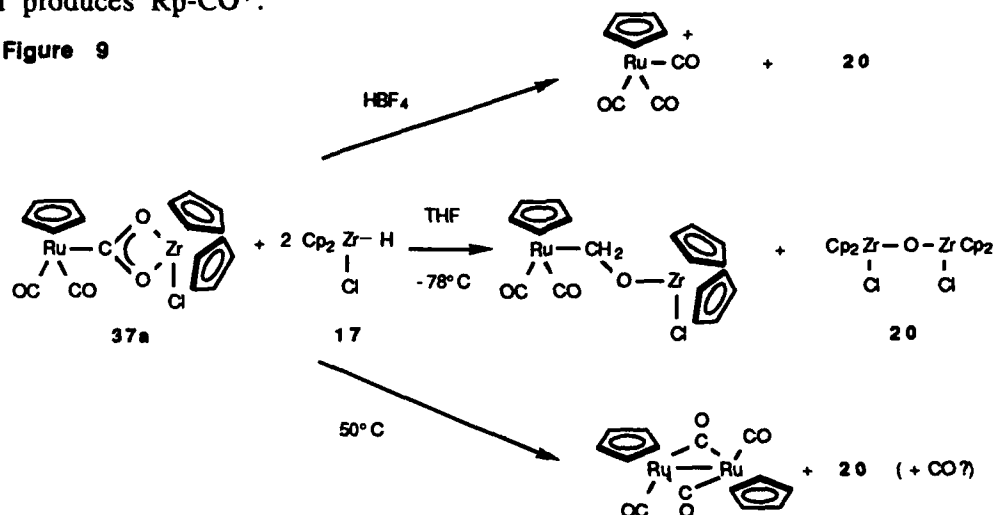


bond on the bridging  $\text{CO}_2$  is a prevailing trend in (1) the thermal decomposition of these bimetallocarboxylates, (2) the protonation of the more stable zirconium adducts 37a and 37c, and (3) the  $\text{Cp}_2\text{Zr}(\text{H})\text{Cl}$  reduction of 37a. This  $\text{RuZr CO}_2$  adduct 37a is the first heterobimetallic  $\text{CO}_2$  complex that has been prepared using  $\text{CO}_2$ .

Conversion of  $\text{RpCO}_2^-$  (36) to its bimetallocarboxylate  $\text{Rp-CO}_2\text{-Zr}(\text{Cl})\text{Cp}_2$  (37a) accomplishes two objectives. First, the relatively high thermal stability of 37a vs 36 confirms the obvious advantage of using two appropriate metals for more effective binding of  $\text{CO}_2$ . Second, the bimetallocarboxylate structure activates the ligated  $\text{CO}_2$  to C-O

cleavage. Warming 37a deoxygenates the CO<sub>2</sub> (Figure 9); we found no evidence for 37a deinserting CO<sub>2</sub> and producing stable Rp-Zr(Cl)Cp<sub>2</sub> (38a). Protonation of 37a also releases  $\mu$ -oxo 20 and produces Rp-CO<sup>+</sup>.

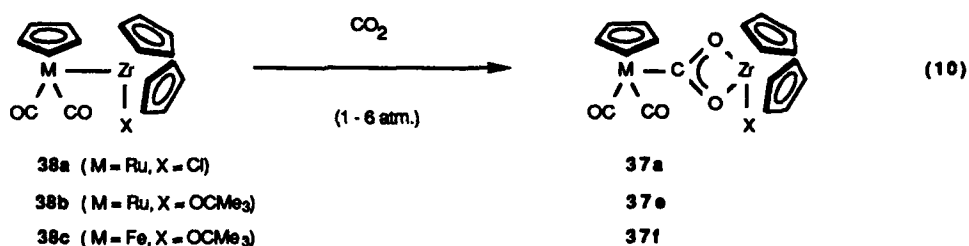
Figure 9



Finally, deoxygenation of 37a occurs upon treating with  $\text{Cp}_2\text{Zr}(\text{H})\text{Cl}$  (17). This reduction cleanly affords the  $\mu(\eta^1\text{-C} : \eta^1\text{-O})$  formaldehyde complex  $\text{Rp}-\text{CH}_2\text{O}-\text{Zr}(\text{Cl})\text{Cp}_2$ .

We were particularly interested in understanding how varying the metal centers M and M' in bimetallic CO<sub>2</sub> complexes  $\text{Cp}(\text{CO})_2\text{M}-\text{CO}_2\text{-M}'(\text{X})\text{Cp}_2$  (37) (eq. 9) and related systems affects their stability as well as their subsequent reactivity. Both zirconocene and titanocene dichlorides  $\text{Cp}_2\text{M}'\text{Cl}_2$  readily transform the iron and ruthenium CO<sub>2</sub> complexes  $\text{Cp}(\text{CO})_2\text{MCO}_2^-$  (24, M = Fe; 36, M = Ru) in THF above  $-40^\circ\text{C}$  to bimetallic  $\mu(\eta^1\text{-C} : \eta^2\text{-O, O'})$  CO<sub>2</sub> adducts 37a-d (eq. 9). Stability of these bimetallocarboxylates, indicated by their relative ease of synthesis and purification, decreases in the order: RuZr (37a)  $\gg$  FeZr (37c)  $>$  RuTi (37b)  $>$  FeTi (37d).

### 3. Insertion of CO<sub>2</sub> into Metal-Metal Bonds



Results of preliminary studies established the differing reactivity of Fe-Zr and Ru-Zr bimetallic complexes  $\text{Cp}(\text{CO})_2\text{M}-\text{Zr}(\text{X})\text{Cp}_2$  (38a-38c) towards CO<sub>2</sub> insertion (eq. 10). The FeZr bimetallic 38c quantitatively reacts within 20 minutes with CO<sub>2</sub> (1 atm.) in THF to generate the  $\mu$ -CO<sub>2</sub> adduct 37f. Unfortunately, 37f decomposes nearly as fast as it forms, although quenching these reactions with HBF<sub>4</sub> affords  $\text{FpCO}^+$  in 25-30% yields (cf. Figure 9). Spectroscopic data for 37f, whether it originates from CO<sub>2</sub> insertion into 38c or from metathesis of  $\text{FpCO}_2^-$  (24) and  $\text{Cp}_2(\text{Me}_3\text{CO})\text{ZrCl}$ , resembles that of 37a and 37c.

Both Ru-Zr bimetallics **38a** and **38b** also insert CO<sub>2</sub>, but at much slower rates. With Rp-(t-butoxy)zirconocene **38b**, for example, CO<sub>2</sub> (6 atm.) converts 85% of it in THF over 3 days to a 3:1 mixture of Rp-CO<sub>2</sub>-Zr(OCMe<sub>3</sub>)Cp<sub>2</sub> (**37e**) and RpH, and one-half of it in toluene over 12 days to a 1:4 mixture. This RpH evidently originates from trace amounts of water in the CO<sub>2</sub>. The formation of stable, fully characterized RuZr bimetalloxy-carboxylates **37a** and **37f** in these CO<sub>2</sub> insertion reactions more than compensates for the relatively low reactivity of the starting Ru-Zr bimetallics. This reaction chemistry is unprecedented.